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PRODUCTION OF ZIRCONIUM BY PLASMA DECOMPOSITION OF ZIRCONIUM TETRACHLORIDE

by

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ABSTRACT

This project deals with a novel application of plasma technology. A transferred-arc plasma of vapour of $ZrCl_4$, obtained by sublimation of the solid tetrachloride, was successfully generated between a specially designed cathode and an anode of molten zirconium. The operating characteristics of this arc were experimentaly compared with those of pure argon. The power used was varied between 10.2 and 30.2 kW. For the range of $ZrCl_4$ feed rates studied, the power increased significantly with arc length, while its dependence on arc current was minor.

The fraction of the input-energy to the system which was transferred to the molten anode by electron transfer decreased almost linearly with an increase in feed rate and an increase in arc length.

The percent of ~~the zirconium originally contained in the feed and converted to zirconium metal~~ conversion of the zirconium fed as the tetrachloride to the zirconium metal in the molten anode varied between 5 and 16.7% and depended strongly on the stability of the arc. Recommendations are made to increase significantly the efficiency of conversion.

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1. INTRODUCTION

The major objective of this project was to demonstrate the technical feasibility of producing dense zirconium metal of nuclear-grade continuously from dehafniated purified zirconium tetrachloride, using a specially-designed plasma system. If successful, this plasma system could replace the whole Kroll Plant in the current conventional industrial process for the production of zirconium sponge from zircon. It has been demonstrated that the Kroll section is the single most expensive part of the whole plant (about 35% of the total operating cost of $6.45 December 1978 Canadian dollars to produce one pound of Zr sponge).

The plasma system is of the transferred arc type, and its design capitalizes on the knowledge and expertise gained by the Plasma Technology Group at McGill during the recent years in this particular area of plasma generation.

Briefly summarized, proposed technique consists of generating vapors of $ZrCl_4$ in a sublimer and of feeding these vapors into a plasma reactor in the form of a transferred arc, where they are decomposed at very high temperatures into zirconium and chlorine ions, and electrons. The ions are neutralized on an anode of molten zirconium metal into which the zirconium atoms will be incorporated, while the reformed chlorine gas leaves the reactor and collected, to be recycled to the system.

The production of metallic zirconium from its halides via the plasma route has received a limited amount of attention in the past. One of the relevant studies on the conversion of the tetrachloride is that of Gragg (1) which confirmed the technical feasibility of producing zirconium, using a 25 kW (nominal) 4MHz R.F. torch. Zirconium tetrachloride vapors at low feed rates (0.4404 to 4.658 g/hour) were fed through a central heated feed tube, upstream of an argon plasma fireball. The argon flow rate was

unfortunately not specified. Conversion ranged from 3.67 to 89.61%, the highest conversion corresponding to the second lowest feed rate of tetrachloride, with consequent impossibly high consumption of electrical energy amounting to 29,500 KWh/kg Zr. The work was very limited in scope and left many questions unanswered.

Surprisingly enough, Gragg appeared to be unaware of the earlier work of Diprieto et al. of the U.S.A. National Research Corporation (2), also reported by Rolsten (3) on the deposition of zirconium from tetraiodide vapors under reduced pressure. This work again demonstrated that the metal could be deposited from the halide vapors at conversion rates up to 97.7%, the highest conversion being obtained at extremely low feed rates.

Indirectly related to the problem is the work of Miller and Ayen (4) on the reduction of titanium tetrachloride vapors in the R.F. torch. Feeding of $TiCl_4$ in an argon plasma resulted in the partial decomposition to the trichloride in good yields, but only when hydrogen was added simultaneously to the torch. No metal was deposited.

It is not surprising that these rather inconclusive earlier results have discouraged further work in this particular field in subsequent years. With a better understanding of the characteristics of thermal plasmas, work appears to have recently resumed. Thus A.A. Ivanov (5) claims that he is now producing zirconium metal from tetraiodide vapors in kilogram quantities, while Akashi and Ohno (6) have recently shown the feasibility of producing titanium metal, albeit at low conversion rates, from titanium tetrachloride vapors introduced, together with some hydrogen, in the tail flame of an argon d.c. jet. These findings should be contrasted with those reported by Miller and Ayen (7).

2. JUSTIFICATION FOR PROPOSED PROCESS

The final steps in the conventional production of zirconium sponge consists in the reduction of dehafniated $ZrCl_4$ vapors in the presence of magnesium (Kroll Process) followed by the vacuum distillation of the pseudoalloy thus obtained (a dispersion of fine Zr powder in an Mg - $MgCl_2$ matrix, analyzing 70% Zr) to remove the magnesium and magnesium chloride.

A recent survey (December 1978) carried out by the Noranda Research Centre for the purpose of reviewing existing technologies for the production of zirconium and of identifying new technologies as the basis for the eventual design of a Canadian production facility, has shown that these two steps - which are of crucial importance to the overall process - involve high operating costs (about 35% of the total operating cost of producing Zr sponge, the latter amounting to $6.45 per pound, according to this recent economic assessment), for the following reasons:

1. They are batch operations, highly labour intensive because they require extreme care against contamination.
2. They require magnesium of very high purity, not all of which can be economically regenerated (about 70% of the excess Mg is recovered as the metal). The net consumption of magnesium is very nearly 1 kg per kg of sponge.
3. The distillation step is carried out under a high vacuum (10^{-3} torr at the end), and the Kroll Process involves the use of large quantities of argon and of some helium.
4. Some zirconium losses are experienced, due to mechanical losses and to contamination.
5. The final stages of sponge shearing, sorting, crushing (with recycling of fines), blending and packaging (or storage) are particularly labour intensive and cause further losses of metal.

Figure 1 illustrates the steps in the conventional industrial batch process, while Figure 2 represents the new proposed (continuous) process. It is evident that the latter, in addition to eliminating the need for magnesium, should also effect considerable savings in capital cost. The production of metal directly into a dense phase in a non-contaminating atmosphere would also provide an additional benefit of great economic significance.

The selection of this approach was based on an analysis of the failures of the previous investigators as follows:

1. Too low and operating temperature. Previous investigators used R.F. plasma torches which develop temperatures of 8,000 K and less. Dissociation of the $ZrCl_4$ molecules only begins at about 3,000 K while that of $ZrCl_2$ becomes appreciable at about 6,000 K (see Figure 3). On the other hand, the average temperature of a transferred arc near the anode, as measured by Mehmetoglu and Choi (8), is about 11,000 K.
2. Dilution with carrier gas. In all previous work, argon was used as the carrier plasmagen gas. In this study, it is proposed to use a plasma of pure $ZrCl_4$ vapors, in the same way that Bicerogly (1978, McGill) developed a plasma of pure chlorine.
3. Improper zirconium collection. All previous investigators collected the zirconium (or titanium) by quenching on a cold surface, ignoring the fact that low temperatures favour the reformation of $ZrCl_4$. It is therefore proposed to collect the neutralized zirconium ions on an anode consisting of molten zirconium metal maintained above the Zr melting point, according to the same technique developed by the Noranda Research Centre for the plasma production of molybdenum.
4. Contamination of metal. Many of the previous investigations were plagued with the contamination of foreign metals from the sublimer, the reactor walls or from the electrodes. It

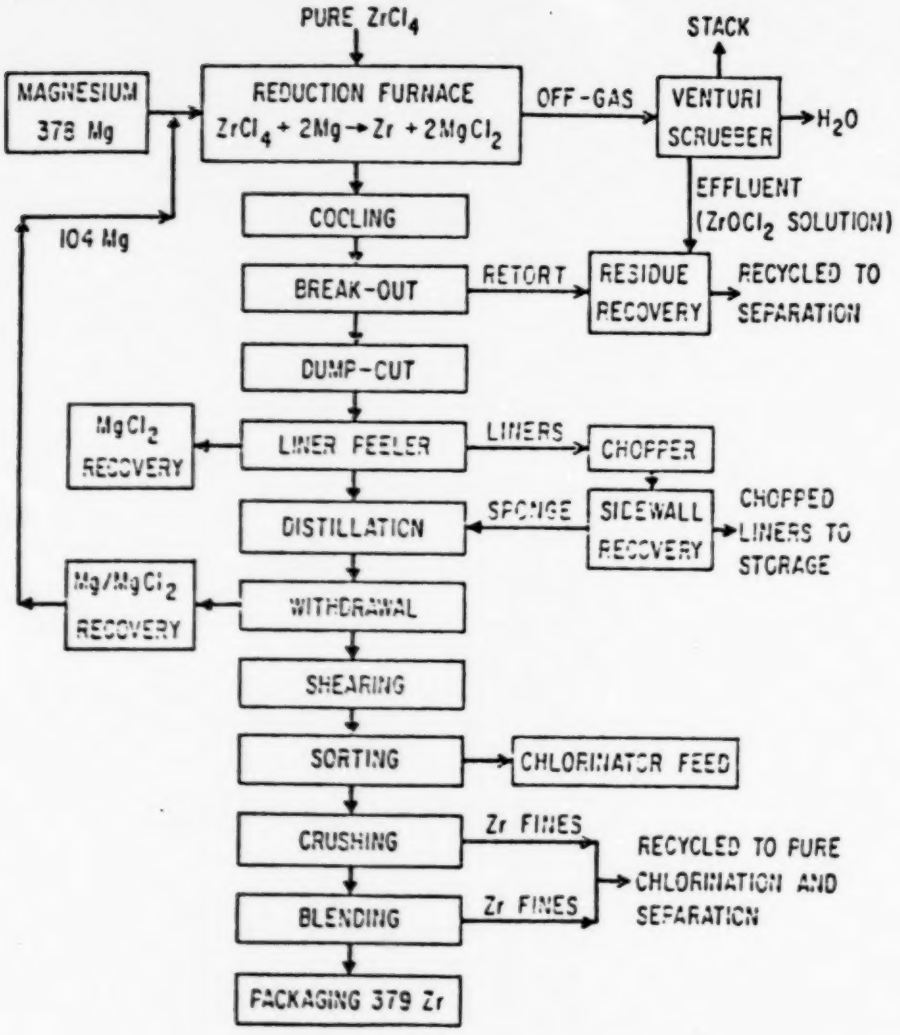

FIGURE 1

Conventional Kroll Process for the Production of Zirconium Sponge

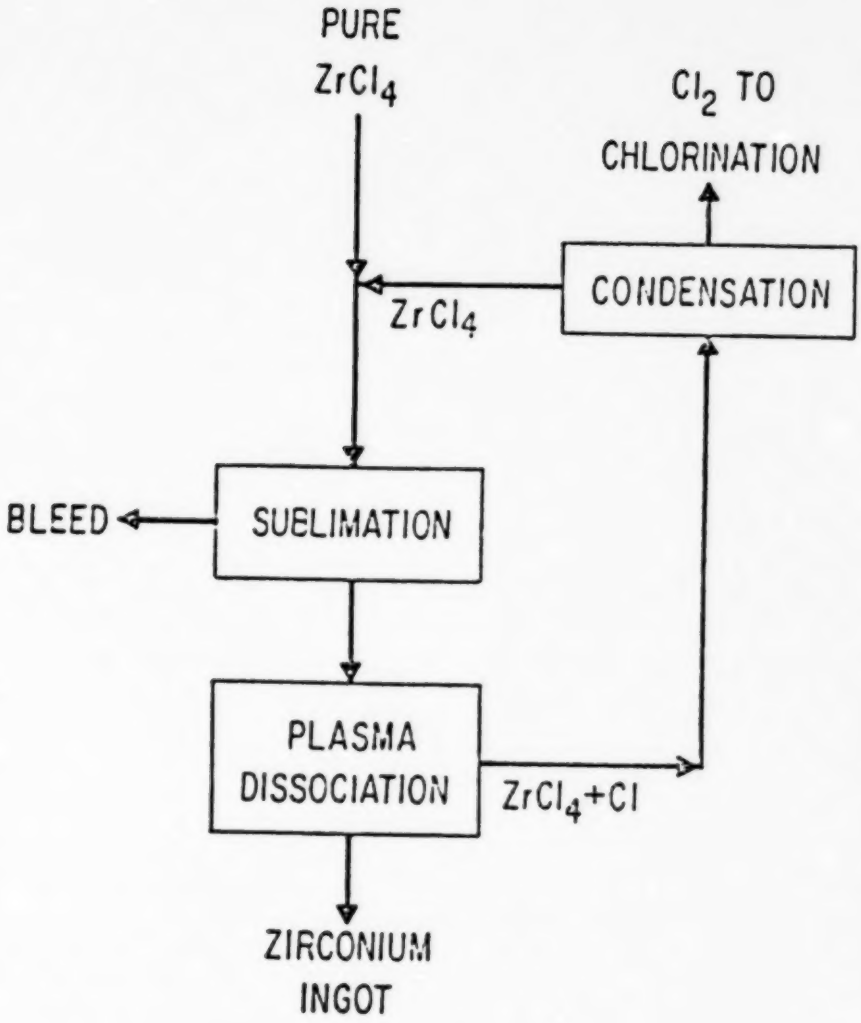

FIGURE 2

Proposed Plasma Process for the Decomposition of Zirconium Tetrachloride

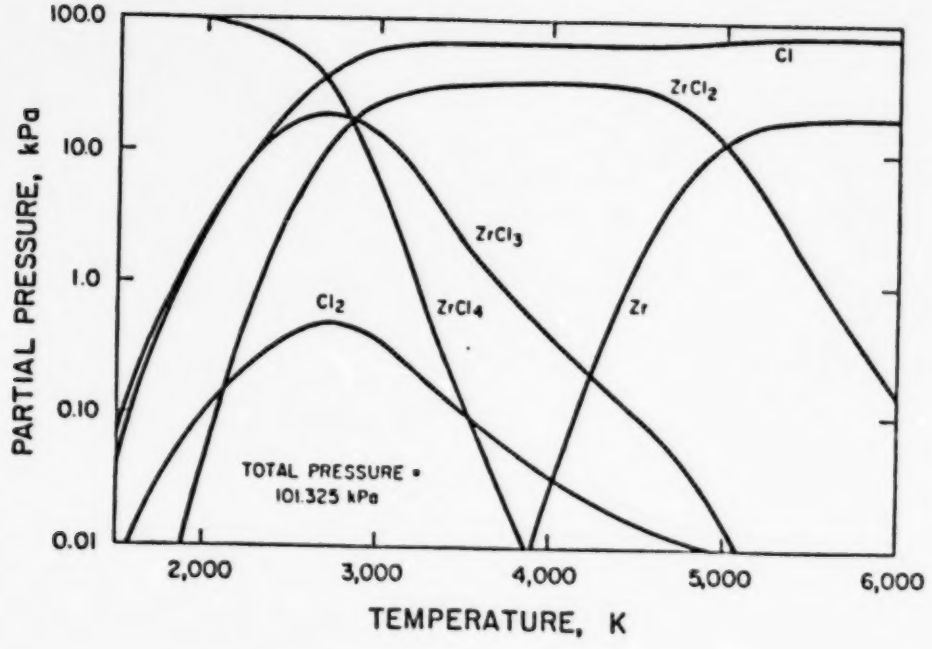

FIGURE 3

Partial Pressure of $ZrCl_4$ and components as a Function of Temperature

is proposed here to use zirconium electrodes, and nickel with mild steel construction, based on previous experience.

It should be mentioned, finally, that the proposed process is designed to produce dense zirconium metal, and not zircomium sponge.

3. EXPERIMENTAL APPARATUS

A schematic diagram of the overall experimental system is shown in Figure 4, and a photograph of the equipment is shown in Figure 5.

Briefly summarized, the experimental apparatus consisted of the following components:

A. The argon electric heater, to heat the whole system to a temperature at all times higher than 331°C, the sublimation temperature of $ZrCl_4$. This was of vital importance, as any condensation of the vapour at any point in the system led to the formation of a rock-hard deposit which usually terminated the experimental run. For this reason all transfer lines (made of ~~nickel-of-~~ monel) were heavily ~~traced~~ with electric tape. Argon was also used to start the arc.

B. The sublimer, consisting of a 12.5 cm diameter Hastelloy C-276 cylinder, 21 cm high, in which the $ZrCl_4$ (previously dehafniated) was sublimed. Originally heated by electrical resistance elements, it was found subsequently that better control of the rate of sublimation could be obtained with a natural gas burner.

C. The cathode assembly, shown in Figure 6. Molybdenum was used for the critical part of the nozzle, close to the plasma. The plasma column, not shown on Figure 6, originated from the cathode tip of thoriated tungsten. The cathode was connected to the negative lead from a 40 kW General Dynamics selenium rectifier (Model TDC IA-40).

D. The reactor chamber consisted of a water-cooled 28.575 cm i.d. 316 stainless steel cylindrical vessel, 21.6 cm in height. Two ports, 5.08 cm in diameter, were provided on the reactor cover to view the plasma column, the molten bath and to

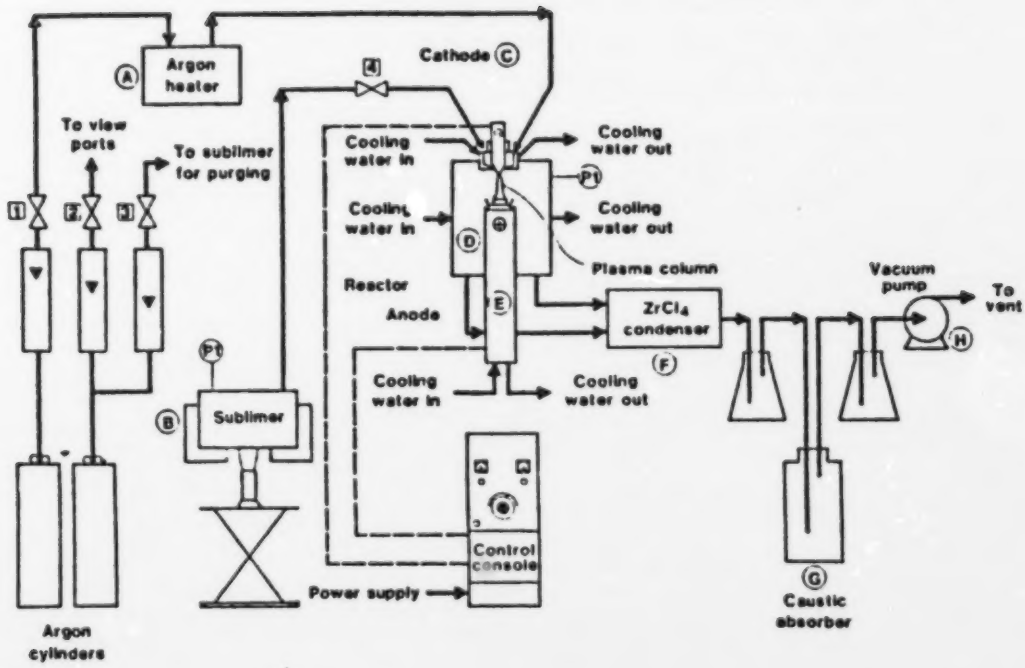

FIGURE 4

Schematic diagram of experimental apparatus

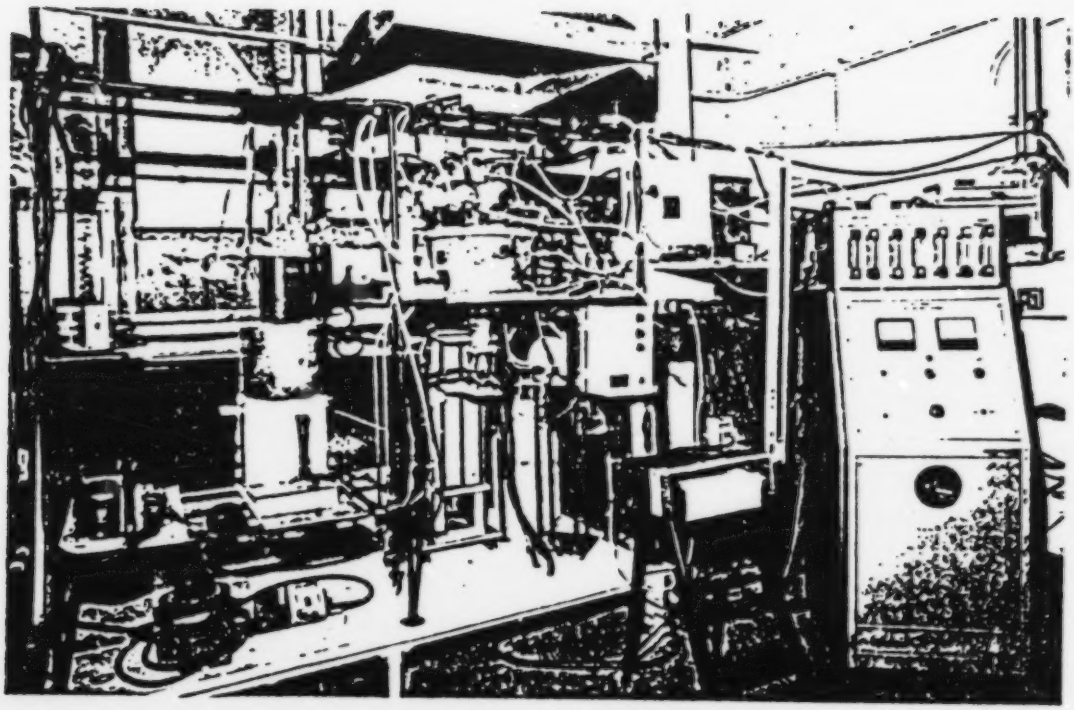

FIGURE 5

Photograph of experimental apparatus

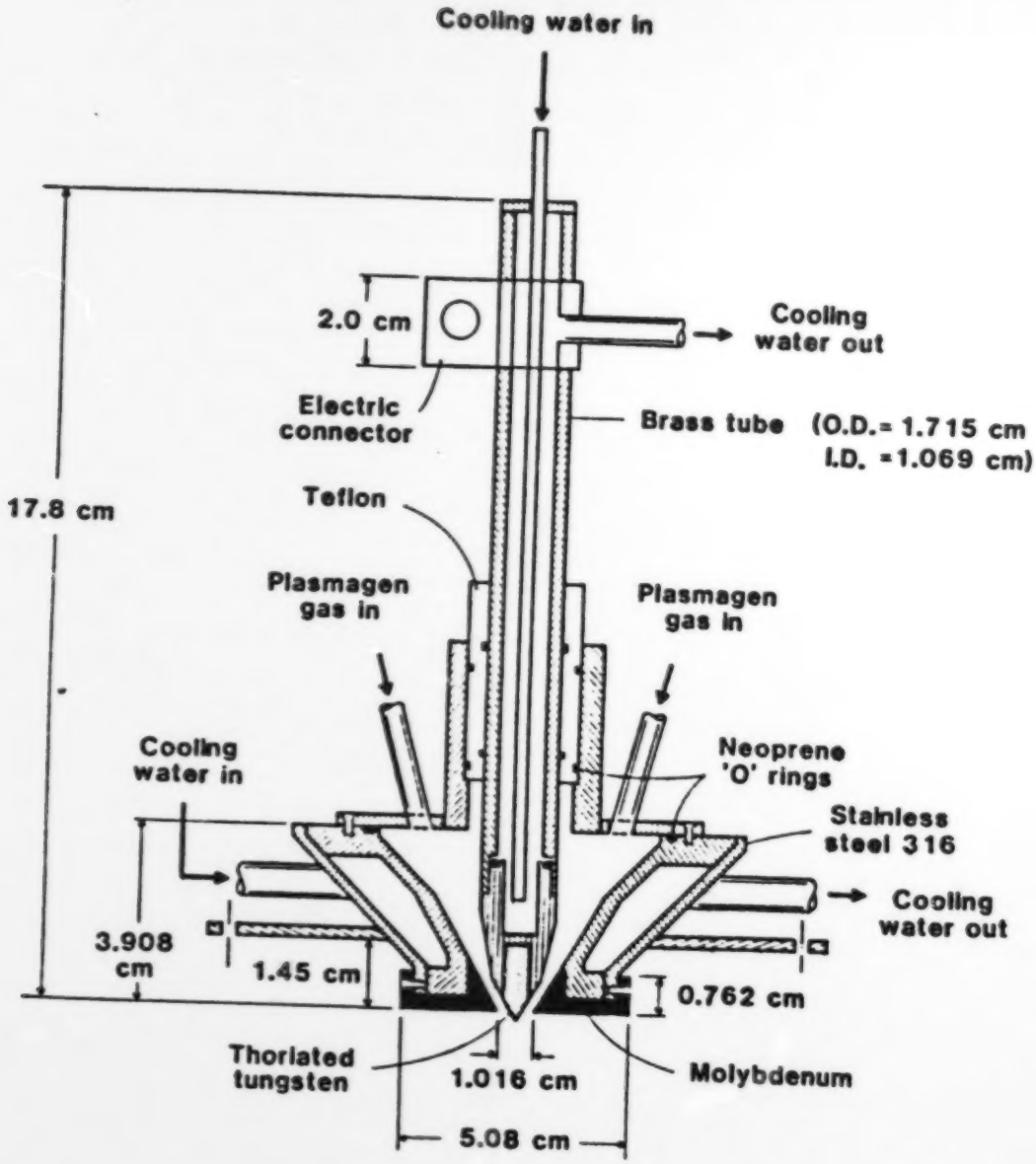

FIGURE 6

Cathode assembly

measure the temperature of the latter by means of an optical pyrometer of high resolution (Pyro Micro-Optical Pyrometer, made by the Pyrometer Instrument Co., Northvale, N.J.).

E. The anode assembly is shown in Figure 7. It was attached at the bottom to a moving platform, remotely driven, which allowed movement of the anode in a vertical direction over a distance of 44 cm. This was necessary to bring the anode in close proximity of the cathode tip (which was fixed in position) in order to start the arc with a H.F. spark. The movement of the anode also permitted the adjustment of the arc to the desired length, once the arc was established.

F,G and H These three components constituted the after-train of the equipment to allow condensation of the untreated $ZrCl_4$ and absorption of the chlorine produced during the conversion of $ZrCl_4$ into zirconium metal. Nickel and stainless steel were the materials of construction used in this part of the system.

4. EXPERIMENTAL RESULTS

Considerable difficulties were at first experienced ~~in~~ establishing a stable plasma column consisting of pure $ZrCl_4$. Once the entire system had been purged ~~of air~~ by means of argon (zirconium metal has a great affinity for oxygen at high temperatures), every line carrying $ZrCl_4$ had to be brought ~~to~~ and maintained at a temperature of at least 350°C to avoid condensation before an argon arc was struck. Transition from an argon plasma to a $ZrCl_4$ was particularly tricky, in view of the much higher ionisation potential required by the latter.

Stability of the arc was of the utmost importance. This could only be maintained at relatively low rates of feed. Near the end of the experimental program, however, a new type of cathode was designed, using tangential entrance for the plasmagen gas which thus

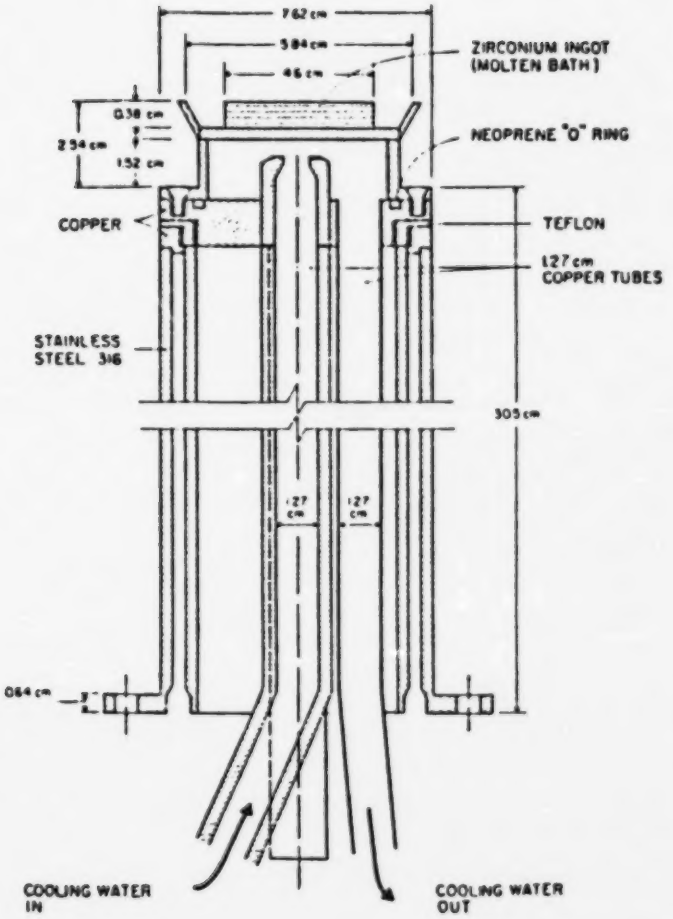

FIGURE 7

Anode assembly

entered the cathode nozzle as a vortex, with a considerable improvement in arc stability. This refinement in technique will be of considerable significance in all subsequent studies of refractory metal systems.

As shown in Figure 8, there was a marked difference in the general appearance of a $ZrCl_4$ arc, when compared with an argon arc (or with a nitrogen arc, studied by Tsantrizos, (9)). The diameter of the luminous arc column in the case of $ZrCl_4$ was much larger, and enlarged considerably near the anode.

As previously stated, one of the major objectives of this project was to obtain the operating characteristics of this entirely new plasma system, so as to provide a basis for pilot-plant development which might hopefully lead to a commercial process. Figure 9 shows the voltage-current relationship for a pure $ZrCl_4$ plasma, at a constant feed rate and for two arc lengths (denoted by the symbol ℓ) of 3 cm and 4 cm respectively. For comparison purposes, data for pure argon are also shown. The much larger potential required by $ZrCl_4$ is at once apparent. It is also significant that the dependence on arc current is not too strong. Figure 10, on the other hand, shows that the arc voltage is much more sensitive to the $ZrCl_4$ flow rate for a constant arc current. This was expected, in view of the considerable energy required to dissociate the $ZrCl_4$ molecule and to achieve some ionization of the zirconium atom.

Figure 11 shows a plot of the total power transferred to the anode as a function of arc current. The effect of the latter was much more important than that of the arc length. A similar behaviour was observed by Tsantrizos (9) for a nitrogen plasma.

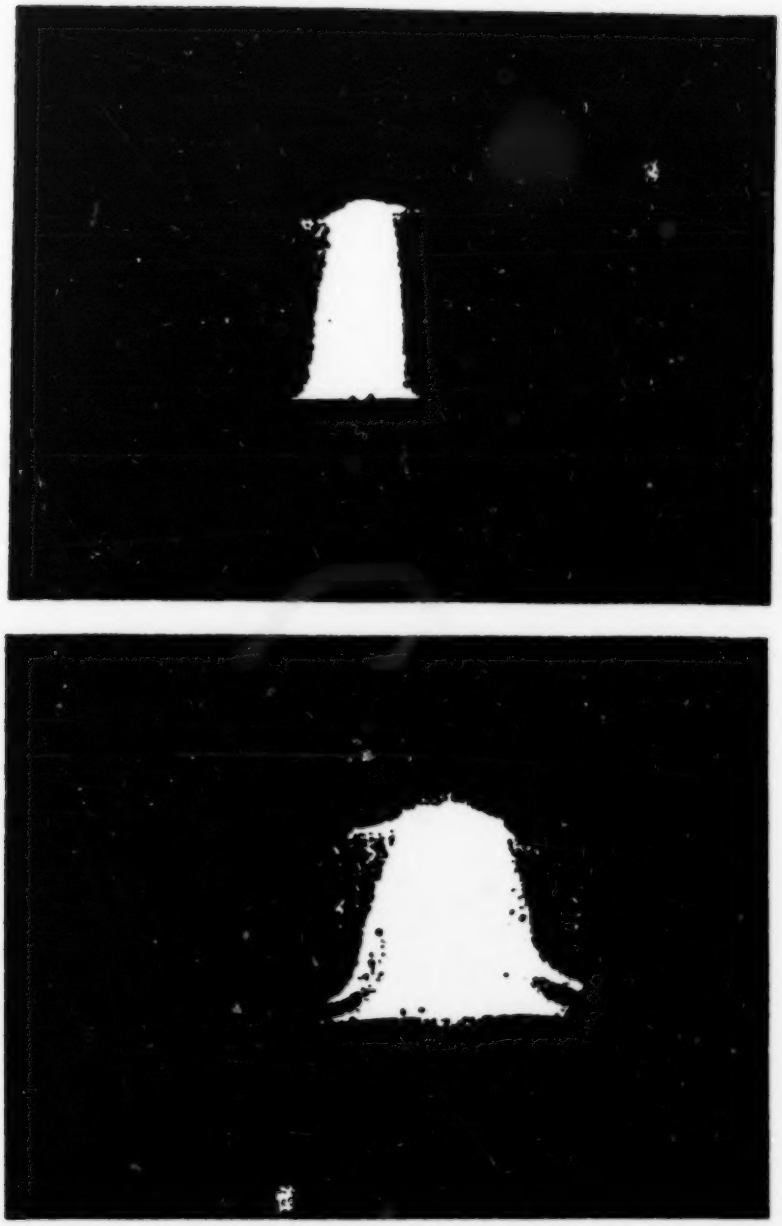

FIGURE 8

Photographs of pure argon (top)
and $ZrCl_4$ (bottom) transferred-arc plasmas

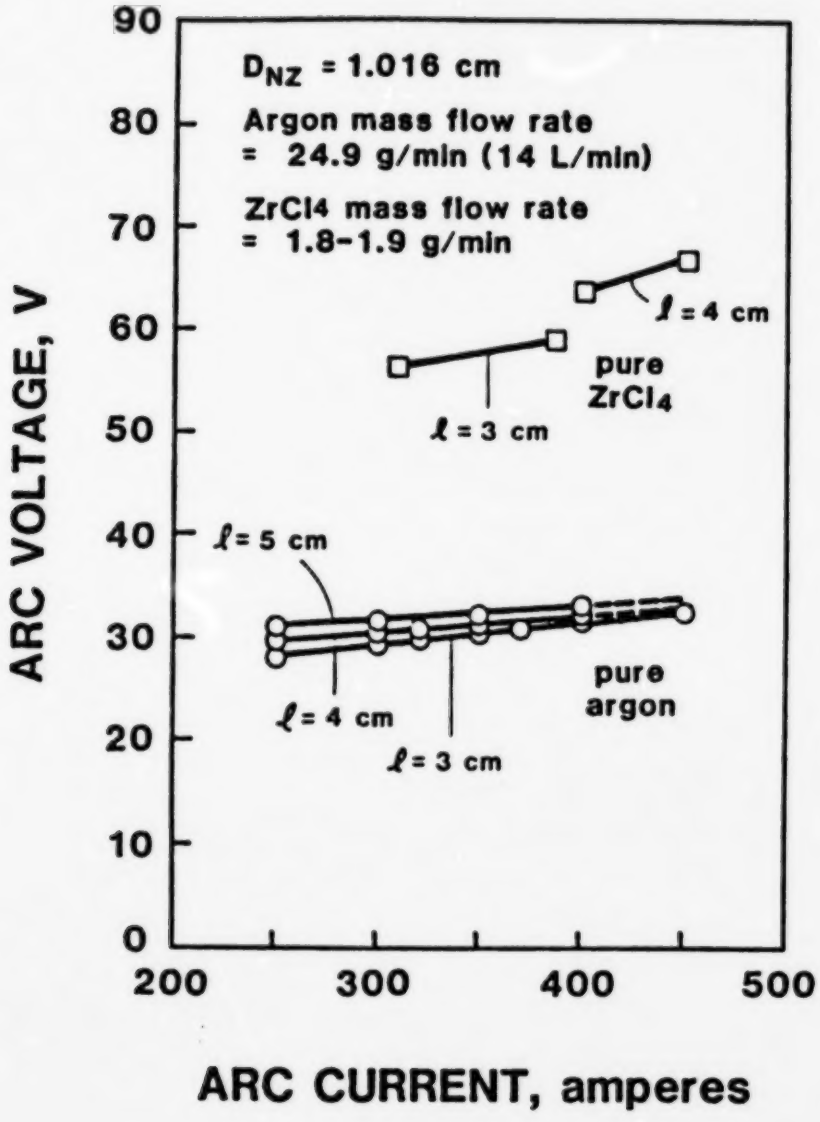

FIGURE 9

Voltage-current relationship for $ZrCl_4$ and argon plasmas

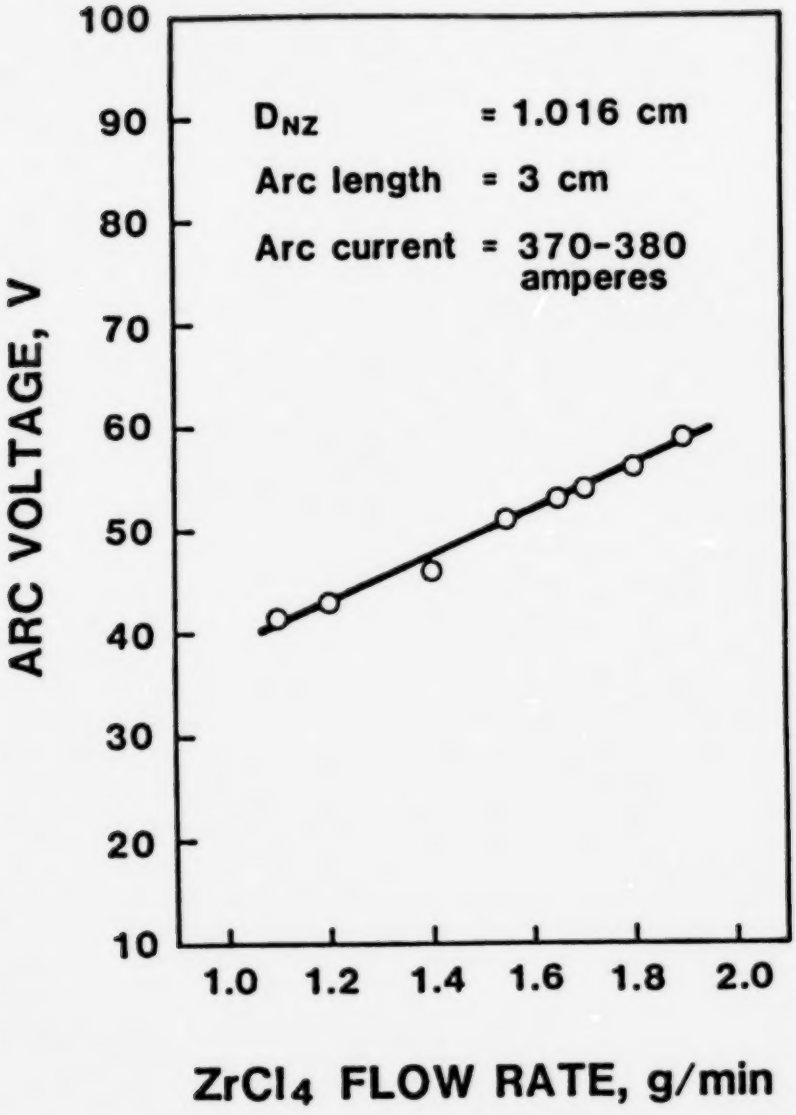

FIGURE 10

Sustained arc voltage variation with $ZrCl_4$ flow rate

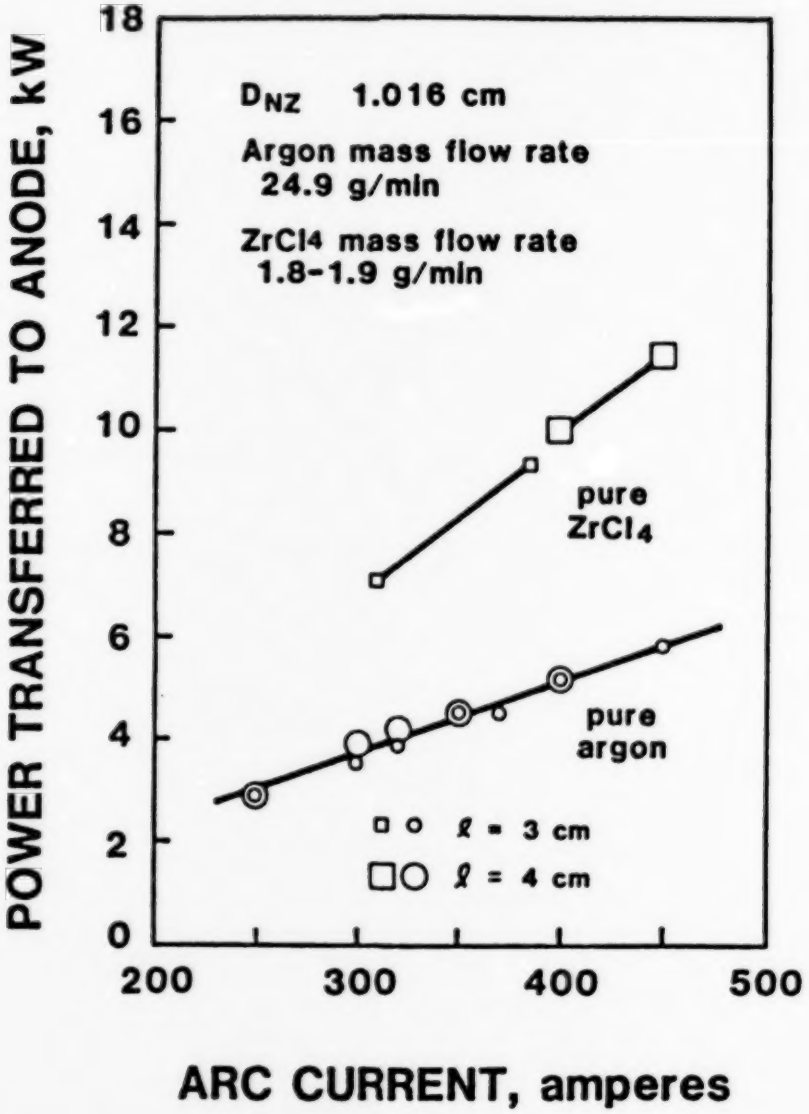

FIGURE 11

Power transferred to the anode as a function of arc current

The effect of $ZrCl_4$ vapour flow rate on the fraction of the power transferred to the anode is shown on Figure 12. It is shown from Choi's work (8) that the electric power fed to the plasma column of a transferred arc goes principally to the anode by electron transfer, and that the rest is radiated to the walls of the reactor. As the resistance of the plasma column increases in the presence of increased $ZrCl_4$, so does the energy necessary to sustain the arc. This means that the energy radiated from the arc must increase, at the expense of the anode transfer, which decreases.

Only 4.2% of the total power was consumed to cool the cathode and the nozzle of the assembly. Pyrometric study of the zirconium molten pool at the centre of the anode showed a central area, about 7 mm in diameter, where a temperature of 2320°C was measured. This is the region where the root of the arc struck most frequently. The rest of the anode was fairly uniform at 2180°C.

Finally, the conversion of the zirconium fed as the tetrachloride to the metal in the anode was determined by direct weighing and was found to range between 5% and 16.7%. The results were not sufficiently reproducible to establish a relationship with the operating conditions, but it was obvious that the degree of conversion was strongly dependent on the stability of the arc.

5. CONCLUSIONS

Based on the results obtained in this study, it can be concluded that the technique, as originally conceived, can indeed produce zirconium metal by collecting it in a molten zirconium anode from a $ZrCl_4$ transferred plasma arc. It is felt that the technical feasibility of the production of the metal has been established, but the optimization of the process for industrial application remains to be accomplished.

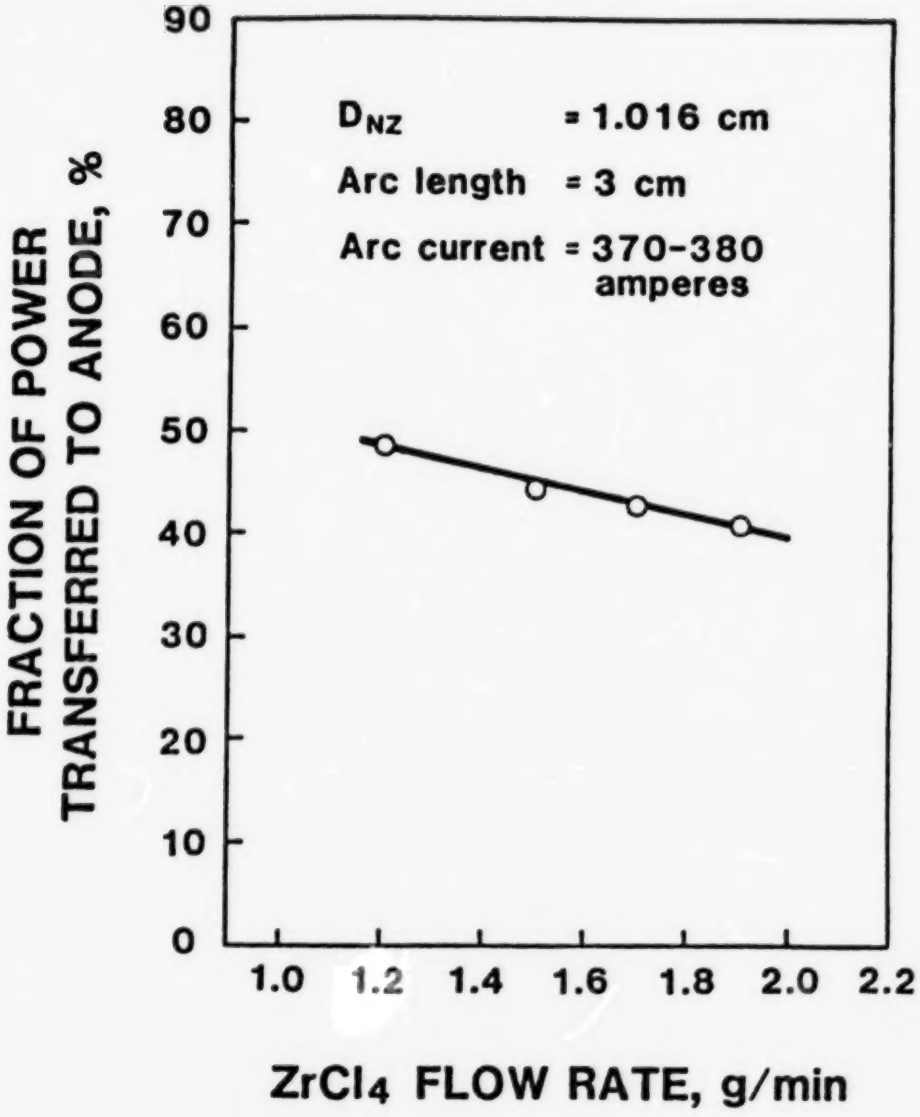

FIGURE 12

Fraction of the total power transferred to the anode, as a function of $ZrCl_4$ flow rate

In this exploratory work, the conversion of zirconium metal in the molten anode ranged from 5 to 16.7%. The conversion was strongly dependent on the stability of the plasma arc, suggesting that a vortex-stabilized arc generated by tangential feeding of the $ZrCl_4$ around the cathode tip should improve conversion significantly. As a matter of fact, a prototype of this novel cathode design has already been designed and built, but not extensively tested. Use of deeper and wider anodes should also be investigated. It should be recalled, as a final conclusion, that the industrial viability of the proposed process does not depend on the complete or near-complete collection in the anode of the zirconium fed to the plasma column. Any zirconium which is not collected will be converted to one of the lower chlorides, and can be recycled to the process feed. Obviously, there will be a minimum conversion rate below which the process is not economically attractive, but the present operating cost of the conventional process is so high that considerable latitude is provided for successful commerciallization of the plasma process.

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